

# IN THE UNEXED STATES PATENT AND TRADEMARK OFFICE

In re Patent of

**TACHIWAMA** 

Atty. Ref.:

330-237

Patent No. 6,818,578 B2

Issued: Nov. 16, 2004

For: OPTICAL GLASS AND PROCESS FOR THE PRODUCTION OF OPTICAL PRODUCTS

\* \* \* \* \*

April 6, 2006

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450 Certificate

APR 1 1 2006

of Correction

Sir:

## REQUEST FOR A CERTIFICATE OF CORRECTION

The patentee in the above-identified patent hereby request that the Patent and Trademark Office issue an official Certificate of Correction pursuant to 37 C.F.R. § 1.323 for the following mistake made by the applicant.

Column 3, line 42, GdO<sub>3</sub> should be Gd<sub>2</sub>O<sub>3</sub>;

Column 6, lines 31, 34, 38 and 41, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

Column 6, line 62, Mgo should be MgO;

Column 7, line 1, Mgo should be MgO;

Column 7, line 32, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

Column 8, line 43, Gd<sub>2</sub>o<sub>3</sub> should be Gd<sub>2</sub>O<sub>3</sub>;

Column 14, line 65, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

04/07/2006 JADDO1 00000133 6818578

Column 15, line 19, Y,Ohd3 should be  $Y_2O_3$ .

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Column 15, line 30,  $ZnO(SiO_2 + B_2O_3)$  should be  $ZnO/SiO_2 + B_2O_3)$ ;

Column 15, line 34, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>.

Column 16, last line, Y,Ohd3 should be Y<sub>2</sub>O<sub>3</sub>;

TACHIWAMA
Patent No. 6,818,578 B2

Column 17, lines 19 and 53, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

Column 17, line 53, B<sub>23</sub> should be B<sub>2</sub>O<sub>3</sub>; and

Column 18, line 20, LiO<sub>2</sub> should be Li<sub>2</sub>O.

Since the error arose on the part of the patentee(s), a check in the amount of \$100.00 is submitted herewith securing issuance of the Certificate.

Attached hereto is a draft Official Certificate of Correction for use by the Patent and Trademark Office correcting the above-identified matter. Also attached is a marked up copy of the patent.

The Commissioner is hereby authorized to charge any <u>deficiency</u> in the fee(s) filed, or asserted to be filed, or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our **Account No. 14-1140**. A <u>duplicate</u> copy of this sheet is attached.

Respectfully submitted,

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#### UNITED STATES PATENT AND TRADEMARK OFFICE

### CERTIFICATE OF CORRECTION

PATENT NO.

: 6,818,578 B2

DATED

: Nov. 16, 2004

INVENTOR(S)

: TACHIWAMA

It is certified that error appears in the above-identified patent and that said letters patent is hereby corrected as shown below:

Column 3, line 42, GdO<sub>3</sub> should be Gd<sub>2</sub>O<sub>3</sub>;

Column 6, lines 31, 34, 38 and 41, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

Column 6, line 62, Mgo should be MgO;

Column 7, line 1, Mgo should be MgO;

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Column 8, line 43, Gd<sub>2</sub>O<sub>3</sub> should be Gd<sub>2</sub>O<sub>3</sub>;

Column 14, line 65, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

Column 15, line 19, Y,Ohd3 should be Y<sub>2</sub>O<sub>3</sub>.

Column 15, line 30,  $ZnO(SiO_2 + B_2O_3)$  should be  $ZnO/SiO_2 + B_2O_3)$ ;

Column 15, line 34, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>.

Column 16, last line, Y,Ohd3 should be Y<sub>2</sub>O<sub>3</sub>;

Column 17, lines 19 and 53, Nb<sub>2</sub>O<sub>3</sub> should be Nb<sub>2</sub>O<sub>5</sub>;

Column 17, line 53, B<sub>23</sub> should be B<sub>2</sub>O<sub>3</sub>; and

Column 18, line 20, LiO<sub>2</sub> should be Li<sub>2</sub>O.

MAILING ADDRESS OF SENDER:

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Arthur R. Crawford

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Tachiwama

# 200年1月31日

JAN. 3 1. 2006 NAKAMORA

PATENT FIRM

# 中村先生

# (12) United States Patent



(10) Patent No.:

US 6,818,578 B2

(45) Date of Patent:

Nov. 16, 2004

#### (54) OPTICAL GLASS AND PROCESS FOR THE PRODUCTION OF OPTICAL PRODUCTS

- (75) Inventor: Kazuo Tachiwama, Hamura (JP)
- (73) Assignce: Hoya Corporation, Tokyo (JP)
- Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 71 days.
- (21) Appl. No.: 09/863,263
- (22) Filed: May 24, 2001
- (65)Prior Publication Data
- US 2002/0006857 A1 Jan. 17, 2002
- Foreign Application Priority Data

May 31, 2000	(JP)	***************************************	2000-16
(51) Int. CL <sup>2</sup>		C03C 3/068+4	man a

- C03C 3/155
- U.S. Cl. ..... 501/78; 501/79; 501/51 (58)Field of Search ...... 501/41, 42, 49-51,
- (56)References Cited

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#### **OTHER PUBLICATIONS**

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\* cited by examiner

Primary Examiner—David Sample Assistant Examiner-Elizabeth A. Bolden (74) Attorney. Agent, or Firm-Nixon & Vandethye P.C.

#### (57)ABSTRACT

An optical glass having high-refractivity and low-dispersion optical properties and having a low glass transition point so that a heat-treating furnace can be operated for a long period of time. The optical glass has a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition point Tg of 700° C, or lower, and contains at least one of La2O2, Gd2O3, Y2O3 or Yb2O3 and at least one of ZrO2, Ta2O5 or Nb2O3, with a weight ratio of the total content of La2O3, Gd2O3, Y2O3 and Yb2O3 to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> of from 3.2 to 5 and the weight ratio of the total content of ZrO2, Ta2O5 and Nb2O5 to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is from 1.1 to 1.5.

26 Claims, No Drawings

贵阶部 GP-0498-US 弊社番号 OOP22007 US

501/55, 63-65, 73, 77-79

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修正にいただますおお願い致はす

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あめせて信正をお願いします

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# OPTICAL GLASS AND PROCESS FOR THE PRODUCTION OF OPTICAL PRODUCTS

#### TECHNICAL BACKGROUND

#### 1. Field of the Invention

The present invention relates to an optical glass, a glass preform made of it, an optical product and a process for the production of the optical product. More specifically, it relates to an optical glass which has high-refractivity and low-dispersion optical properties, has a low glass transition point and allows the stable operation of a heat-treating furnace for a long period of time, a glass preform which is made of the above optical glass and suitable for the formation of various optical products, an optical product made of the above optical glass, and a process for the production of the above optical product.

#### 2. Explanation of Related Art

Conventionally, an optical glass having high-refractivity and low-dispersion optical properties contains a large amount of La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, etc., for attaining a high refractive index and a low dispersion property as is shown, for example, in JP-A-54-90218 and JP-B-54-6042, and glass-network-forming components such as B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are contained in a small amount, so that the above optical glass is extremely highly liable to undergo crystallization. Since a glass that can be stably produced is limited in compositional range, commercially available optical glasses having a high refractive index and a low dispersion have a glass transition point Tg of over 720° C. Table 1 shows properties of high-refractivity low-dispersion optical glasses shown in brochures supplied by optical glass manufacturers.

TABLE 1

	Refractive index (nd)	Abbe's gumber [vd]	Glass trapsi- tion point [Tg] (" C.)
A	1.88300	÷0.3	730
₿.	1.88057	41.01	758
C	1.88300	40.8	738

Conventional high-refractivity low-dispersion glasses have a very high temperature for viscous flows as is typically shown by glass transition points Tg, and for example, annealing treatment thereof has required a temperature of 710° C. or higher. Generally, most of firmaces for glass annealing are made of a stainless steel plate, and this material has a deformation temperature around 700° C. When the annealing is carried out at a temperature over 710° C., therefore, there is caused a problem that the above stainless steel plate undergoes deformation, so that it is difficult to operate the furnace for a long period of time.

Further, the production of a lens material by re-heat pressing also requires a very high temperature, which causes a heat-treating furnace to deteriorate scorner and hinders stable production.

Meanwhile, when a glass has a glass transition point Tg 6a of 700° C, or lower, stable production has been achieved without causing any special load on the operation of facilities.

#### SUMMARY OF THE INVENTION

Under the circumstances, it is a first object of the present invention to provide an optical glass that has high-

refractivity low-dispersion optical properties, has a low glass transition point and allows the stable operation of a heat-treating furnace for a long period of time.

It is a second object of the present invention to provide a glass preform that is made of the above optical glass and is suitable for forming various optical products, and an optical product made of the above optical glass.

It is a third object of the present invention to provide a process for efficiently producing an optical product made of the above optical glass.

For developing optical glasses having the above desirable properties, the present inventors have made diligent studies with regard to effects of compositions of components constituting glasses on optical properties, thermal properties and devirtification resistance. As a result, it has been found that an optical glass having high-refractivity and low-dispersion optical properties and having a glass transition point of 700° C. or lower can be obtained by controlling the ratio of the total content of La<sub>2</sub>O<sub>5</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub>, and the ratio of the total content of ZrO<sub>2</sub>. Ta<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>3</sub>, to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> such that the above ratios come into specific ranges, or by forming a glass having a specific glass composition, and that the first object of the present invention can be accordingly achieved.

Further, it has been also found that the above second object of the present invention can be achieved by a glass preform and an optical product made of the above optical glass each.

It has been further found that a optical product made of the above optical glass can be efficiently produced by employing a specific step, and that the above third object of the present invention can be accordingly achieved.

The present invention has been completed on the basis of the above findings. That is, the present invention provides:

- (1) an optical glass having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition point Tg of 700° C, or lower (to be referred to as "optical glass I of the present invention" hereinafter),
- (2) an optical glass which is a borosilicate glass comprising at least one selected from  $La_2O_3$ ,  $Gd_2O_3$ ,  $Y_2O_3$  or  $Yb_2O_3$  and at least one selected from  $ZrO_2$ ,  $Ta_2O_3$  or  $Nb_2O_3$ , wherein the ratio (weight ratio) of the total content of  $La_2O_3$ ,  $Gd_2O_3$ ,  $Y_2O_3$  and  $Yb_2O_3$  to the total content of  $SiO_2$  and  $B_2O_3$  is from 3.2 to 5 and the ratio (weight ratio) of the total content of  $ZrO_2$ ,  $Ta_2O_3$  and  $Nb_2O_3$  to the total content of  $SiO_2$  and  $B_2O_3$  is from 1.1 to 1.5, and which has a refractive index nd of at least 1.875 and an Abbe's number vd of at least 39.5 (to be referred to as "optical glass II of the present invention" bereinafter),
- (3) an optical glass which is a borosilicate glass comprising at least one selected from La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>5</sub> or Yb<sub>2</sub>O<sub>3</sub>, at least one selected from ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub> and ZnO, wherein the ratio (weight ratio) of the total content of La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>5</sub>, Y<sub>2</sub>O<sub>5</sub> and Yb<sub>2</sub>O<sub>5</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is from 2 to 5, the ratio (weight ratio) of the total content of ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is from 0.5 to 3 and the ratio (weight ratio) of ZnO to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is at least 0.14, and which has a refractive index nd of at least 1.875 and an Abbe's number vd of at least 39.5 (to be referred to as "optical glass III of the present invention" hereinafter).
- (4) an optical glass having a glass composition comprising, by % by weight, 3 to 10% of SiO<sub>2</sub>, 7 to 15% of B<sub>2</sub>O<sub>3</sub>, 30 to 60% of La<sub>2</sub>O<sub>3</sub>, 2 to 8% of ZrO<sub>2</sub> and 13 to 19% of Ta<sub>2</sub>O<sub>4</sub>, wherein the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is 14

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to 20% and the total content of the above components is at least 95% (to be referred to as "optical glass IV of the present invention" hereinafter).

- (5) a glass preform made of any one of the above glasses I to IV.
- (6) an optical product made of any one of the above classes I to IV.
- (7) a process for the production of an optical pracher made of any one of the above optical glasses I to IV, which comprises the steps of melting raw materials for glass and directly press-molding a molten glass, and
- (8) a process for the production of an optical product, which comprises the steps of softening a glass preform made of any one of the above optical glasses. I to IV under heat and press-molding the glass preform softened under heat.

# PREFERRED EMBODIMENTS OF THE INVENTION

The optical glass of the present invention includes four 20 embodiments, i.e., four optical glasses I to IV.

First, the optical glass I is a high-refractivity low-dispersion optical glass having a low glass transition point and having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition point Tg of 25 700° C, or lower.

The above optical glass I preferably includes a borosilicate glass containing at least one selected from  $La_2O_3$ ,  $Gd_2O_3$ ,  $Y_2O_3$  or  $Yb_2O_3$  and at least one selected from  $ZrO_2$ ,  $Ta_2O_5$  or  $Nb_2O_5$ , wherein the weight ratio of the total content of  $La_2O_3$ ,  $Gd_2O_3$ ,  $Y_2O_3$  and  $Yb_2O_3$  to the total content of  $SiO_2$  and  $B_2O_3$  is from 2 to 4, and the weight ratio of the total content of  $ZrO_2$ ,  $Ta_2O_5$  and  $Nb_2O_5$  to the total content of  $SiO_2$  and  $B_2O_3$  is from 1 to 2.

In the composition of the above optical glass I, when the weight ratio of the total content of La2O3, Gd2O3, Y2O3 and Yb<sub>2</sub>O<sub>3</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> [(La<sub>2</sub>O<sub>3</sub>+  $Gd_2O_3+Y_2O_5+Yb_2O_3)/(SiO_2+B_2O_3)$  is less than 2, it is difficult to obtain an optical glass having a high refractive 40 index and a high Abbe's number, which is one of the objects of the present invention. The content of ZnO that improves dispersion as compared with La2O, and GdO, Is limited, and as a result, it is difficult to obtain an optical glass having a glass transition point sufficient for mass-productivity. On the other hand, when the above weight ratio exceeds 4, the devitrification resistance is poor, so that it is difficult to obtain a stably mass-producible glass. Therefore, the weight ratio of the total content of La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> to the total content of SiO2 and B2O3 is preferably in the range of from 2 to 4, more preferably 3 to 4, still more preferably 3.1 to 3.7.

Further, when the weight ratio of the total content of  $ZrO_2$ ,  $Ta_2O_5$  and  $Nb_2O_5$  to the total content of  $SiO_2$  and  $B_2O_3[(ZrO_2+Ta_2O_5+Nb_2O_5)/(SiO_2+B_2O_2)]$  is less than 1, it is difficult to obtain an optical glass having a high refractive index intended in the present invention and stability sufficient for mass-productivity. On the other hand, when it exceeds 2, the Abbe's number vid decreases, and it is difficult to obtain a low-dispersion optical glass that is an end product of the present invention. Therefore, the weight ratio of the total content of  $ZrO_2$ ,  $Ta_2O_5$  and  $Nb_2O_5$  to the total content of  $SiO_2$  and  $B_2O_3$  is preferably in the range of from 1 to 2, more preferably 1.1 to 1.5, still more preferably 1.2 to 1.4.

The above optical glass I may further contain ZnO. The ss weight ratio of the content of ZnO to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> [ZnO/(SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>)] is preferably more than

0 but not more than 2, more preferably more than 0 but not more than 1, particularly preferably 0.1 to 0.5. When the [ZnO/(SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>)] weight ratio is in the above range, the glass can be imparted with properties of high refractivity and low dispersion (the dependency of a refractive index on a wavelength is small), and further, the glass can be improved in devirtification resistance and the temperature for the viscous flow thereof can be decreased.

As a preferred composition, the optical glass I of the present invention has a glass composition (a) comprising, by % by weight, 3 to 10% of SiO<sub>2</sub>, 7 to 15% of B<sub>2</sub>O<sub>3</sub>, 0 to 5% of GeO<sub>2</sub>, 0 to 15% of ZnO, 30 to 60% of La<sub>2</sub>O<sub>3</sub>, 0 to 30% of Gd<sub>2</sub>O<sub>3</sub>, 0 to 10% of Y<sub>2</sub>O<sub>3</sub>, 0 to 5% of Yb<sub>2</sub>O<sub>3</sub>, 2 to 8% of ZrO<sub>2</sub> and 13 to 19% of Ta<sub>2</sub>O<sub>3</sub>, wherein the total content of SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> is 14 to 20% by weight, the total content of B<sub>2</sub>O<sub>3</sub> and ZnO is at least 9% by weight and the total content of La<sub>2</sub>O<sub>3</sub>,  $Gd_2O_3$ , Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> is 50 to 60% by weight, and further wherein the total content of the above components exceeds 95% by weight, and the composition contains 0 to 1% by weight of Li<sub>2</sub>O and 0 to 3% of Nb<sub>2</sub>O<sub>3</sub>.

In the above glass composition, SiO<sub>2</sub> is a glass-network-forming component essential for maintaining devitrification resistance, and the content thereof is preferably in the range of from 3 to 10% by weight. When the above content is less than 3% by weight, the devitrification resistance is insufficient. When it exceeds 10% by weight, the refractive index decreases. It is therefore difficult to obtain a high-refractivity optical glass that is an end product of the present invention. In view of the devitrification resistance and the refractive index, the content of SiO<sub>2</sub> is preferably in the range of from 6 to 9% by weight, more preferably 6.5 to 8.5% by weight.

 $B_2O_3$  is a component having an effect as a network-forming oxide or an effect on meltability of the glass and a decrease in the temperature for viscous flow, and the content thereof is preferably in the range of from 7 to 15% by weight. When the content of  $B_2O_3$  is less than 7% by weight, the effect on meltability of the glass and a decrease in the temperature for viscous flow is not sufficient. When it exceeds 15% by weight, the refractive index of the glass decreases. It is therefore difficult to obtain a high-refractivity glass that is an end product of the present invention. In view of the effect on the meltability of the glass and a decrease in the temperature for viscous flow and the refractive index, the content of  $B_2O_3$  is more preferably in the range of from 9 to 12% by weight, still more preferably 9.5 to 11% by weight.

 $GeO_2$  has the same effect as that of the above  $SiO_2$ , and may be incorporated in an amount in the range of from 0 to 5% by weight. When the content thereof exceeds 5% by weight, the devirtification resistance is liable to decrease.

The total content of the above SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> is preferably in the range of from 14 to 20% by weight. When the above total content is less than 14% by weight, the crystallization tendency increases in intensity, so that it is difficult to obtain an optical glass that can be stably produced. When it exceeds 20% by weight, the refractive index decreases, so that it is difficult to obtain a high-refractivity optical glass that is an end product of the present invention. In view of the crystallization tendency and the refractive index, the above total content of the above SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and GcO<sub>2</sub> is more preferably in the range of from 16 to 19% by weight, still more preferably 16 to 18% by weight.

ZnO works to impart the glass with a high refractive index and low dispersion (the dependency of a refractive index on a wavelength is small), and further, it works to improve the glass in devitrification resistance and to decrease the tem-

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perature for the viscous flow. ZnO is therefore a component that is added as required after its amount is adjusted particularly by taking account of the amount of B2O3. Specifically,  $(SiO_2+B_2O_3)$ :ZnO: $(La_2O_3+Gd_2O_3+Y_2O_3+$ Yb<sub>2</sub>O<sub>3</sub>):(Nb<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub>+Ta<sub>2</sub>O<sub>3</sub>) is adjusted to impart the 5 glass with a refractive index od of at least 1.875 and an Abbe's number vd of at least 39.5 and also with devitrification resistance feasible for glass production, and the total content of B2O2 and ZnO is adjusted preferably to at least 9% by weight, more preferably to at least 12% by weight, whereby the temperature for viscous flow can be decreased (Tg is 700° C, or lower). The content of ZnO is advantageously in the range of from 0 to 15% by weight. When the content of ZnO exceeds 15% by weight, the devitrification resistance may be insufficient in an attempt to obtain a 15 refractive index in the intended range. On the other hand, when an attempt is made to maintain the devitrification resistance feasible for stable production, the refractive index decreases. It is therefore difficult to obtain a high-refractivity optical glass that is an end product of the present invention. 20 The content of ZnO is more preferably in the range of 1 to 7% by weight, still more preferably 3 to 5% by weight.

La<sub>2</sub>O<sub>3</sub> is an essential component for obtaining a high-refractivity low-dispersion optical glass, and the content thereof is preferably in the range of from 30 to 60% by weight. When the above content is less than 30% by weight, it is difficult to obtain an intended high-refractivity low-dispersion optical glass, and when it exceeds 60% by weight, the devitrification resistance decreases, so that it is difficult to obtain a glass that can be stably produced. The 32 above content is more preferably in the range of from 37 to 48% by weight, still more preferably 40 to 45% by weight.

 $Gd_2O_3$  may be incorporated in an amount range of from 0 to 30% by weight as a substitute for  $La_2O_3$ . When the above content exceeds 30% by weight, the devitrification resistance decreases, so that it is difficult to obtain a glass that can be stably produced. The above content is more preferably in the range of from 0 to 18% by weight, still more preferably 5 to 15% by weight.

 $Y_2O_3$  and  $Yb_2O_3$  may be also incorporated in the amount range of from 0 to 10% by weight and 0 to 5% by weight, respectively, as a substitute for the above  $La_2O_3$ . When the content of  $Y_2O_3$  exceeds 10% by weight, or when the content of  $Yb_2O_3$  exceeds 5% by weight, the devitrification resistance decreases, so that it is difficult to obtain a glass that can be stably produced. The content of  $Y_2O_3$  is more preferably in the range of from 0 to 6% by weight, still more preferably 3 to 6% by weight. Further, the content of  $Yb_2O_3$  is more preferably in the range of from 0 to 5% by weight, still more preferably 0 to 2% by weight.

The above La<sub>2</sub>O<sub>3</sub> and the above Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> have similar effects on optical properties, and preferably, the total content of these components is in the range of from 50 to 60% by weight. When the above total content is less than 550% by weight, it is difficult to obtain a high-refractivity low-dispersion optical glass that is an end product of the present invention. When it exceeds 60% by weight, the devitrification resistance decreases, so that it is difficult to obtain a glass that can be stably produced. The above total 62 content is more preferably in the range of from 51 to 58% by weight, still more preferably 54 to 56% by weight.

ZrO<sub>2</sub> is a component for attaining a high refractive index, and it exhibits an effect on improving the devitrification resistance when incorporated in a small amount. The content 65 thereof is preferably in the range of from 2 to 8% by weight. When the above content is less than 2% by weight, it is

difficult to obtain a high-refractivity optical glass, and ZrO<sub>2</sub> may fail to exhibit the effect on fully improving the devit-rification resistance. When the above content exceeds 8% by weight, the devirrification resistance may rather decrease and the glass transition point may increases, so that it may be difficult to achieve the object of the present invention. The above content is more preferably in the range of from 4 to 8% by weight, still more preferably 4 to 6% by weight.

Ta<sub>2</sub>O<sub>5</sub> is an essential component for attaining the high-refractivity, and the content thereof is preferably in the range of from 13 to 19% by weight. When the above content is less than 13% by weight, it is difficult to obtain a high-refractivity optical glass that is an end product of the present invention. When it exceeds 19% by weight, not only the devitrification resistance may decrease, but also the transmittance absorption end may shift toward a longer wavelength side. The above content is more preferably in the range of from 13 to 17% by weight, still more preferably 14 to 17% by weight.

In the optical glass I of the present invention, preferably, the total content of  $SiO_{2}$ ,  $B_{2}O_{5}$ ,  $GeO_{2}$ , ZnO,  $La_{2}O_{3}$ ,  $Gd_{2}O_{3}$ ,  $Y_{2}O_{3}$ ,  $Yb_{2}O_{5}$ ,  $ZrO_{2}$  and  $Ta_{2}O_{5}$  exceeds 95% by weight. When the above total content is less than 95% by weight, it is difficult to obtain an optical glass that satisfies all of the optical properties, the decrease in temperature for viscous flow and the devitrification resistance that are intended in the present invention. The above total content is more preferably at least 96% by weight, still more preferably at least 98% by weight.

In addition to the above components, the optical glass for the present invention may contain (Nb<sub>2</sub>O<sub>3</sub>) WO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, BaO, SrO, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, Li<sub>2</sub>O and Sb<sub>2</sub>O<sub>3</sub> as required.

Nb.O. and WO<sub>3</sub> are components for improving the devitrification resistance when incorporated in a small amount.
Each of these components may be incorporated in an amount
range of from 0 to 2% by weight. When the content of
Nb<sub>2</sub>O. exceeds 3% by weight, or when the content of WO<sub>3</sub>
exceeds 3% by weight, the absorption of the class in the
shorter wavelength region is intensified, which causes the
glass to be colored. The content of Wb<sub>2</sub>O<sub>3</sub> is more preferably
in the range of from 0 to 1.5% by weight, still more
preferably 0.5 to 1.5% by weight. Further, the cantent of
WO<sub>3</sub> is more preferably in the range of from 0 to 2% by
weight, still more preferably 0 to 1% by weight.

 $Bi_2O_3$  is a component having an effect on decreasing Tg when incorporated in a small amount, and it may be incorporated in an amount range of from 0 to 3% by weight. When the content of  $Bi_2O_3$  exceeds 3% by weight, it decreases the devitrification resistance or causes the glass to be colored. The content thereof is more preferably in the range of from 0 to 2% by weight, still more preferably 0 to 1% by weight.

 $Al_2O_3$  and  $Ga_2O_3$  may work to improve the devirtification resistance in some cases when incorporated in a small amount. However, they also work to decrease the refractive index. The content of each of these components is preferably in the range of from 0 to 3% by weight. The content of  $Al_2O_3$  is more preferably in the range of from 0 to 2.5% by weight, still more preferably 0 to 0.5% by weight.

BaO, SrO, CaO and Mgo have an effect on promoting defoaming when used in the form of carbonates or nitrates as raw materials for the glass. However, when the total content of these components exceeds 3% by weight, the devitrification resistance decreases, so that it is difficult to obtain an optical glass that can be stably produced. The total

2)

Nb205

3

Mg O

content of BaO, SrO, CaO and Mgo is therefore preferably in the range of from 0 to 3% by weight. The content of BaO is more preferably in the range of from 0 to 2% by weight, still more preferably 0 to 1% by weight. The content of SrO is more preferably in the range of from 0 to 2% by weight, s still more preferably 0 to 1% by weight.

Na<sub>2</sub>O, K<sub>2</sub>O and Li<sub>2</sub>O have an effect on decreasing the glass transition point Tg, and Li-O in particular has a very high effect on such. However, these components function as a great factor for decreasing the devitrification resistance and the refractive index. The total content of Na<sub>2</sub>O, K<sub>2</sub>O and Li<sub>2</sub>O is preferably in the range of from 0 to 1% by weight. The content of LiO is more preferably in the range of from 0 to 0.5% by weight.

Sb<sub>2</sub>O<sub>3</sub> as a refining agent may be incorporated in an <sup>35</sup> amount range of from 0 to 1% by weight. The above refiring agent Sb<sub>2</sub>O<sub>2</sub> may be replaced with other refining agent such ss SnO<sub>2</sub>. The content of Sb<sub>2</sub>O<sub>3</sub> is preferably in the range of from 0 to 0.5% by weight.

As another preferred composition, the optical glass I of 20 the present invention has a glass composition (b) comprising, by % by weight, 5 to 10% of SiO., 7 to 13% of  $B_2O_3$ , 0 to 5% of  $GeO_2$ , 0 to 15% of ZnO, 30 to 60% of 1,2,0,0 to 30% of Gd2O2, 0 to 5% of Y2O2, 0 to 5% of Yb<sub>2</sub>O<sub>3</sub>, 2 to 8% of ZrO<sub>2</sub> and 13 to 19% of Ta<sub>2</sub>O<sub>5</sub>, wherein the total content of SiO2, B2O3 and GeO2 is 14 to 20% by weight, the total content of B2O3 and ZnO is at least 9% by weight and the total content of La<sub>2</sub>O<sub>5</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> is 50 to 60% by weight, and further wherein the total content of the above components exceeds 95% by weight, the composition further contains, by % by weight, 0 to 3% of (Nb2O2)0 to 3% of WO3, 0 to 3% of Al2O2, 0 to 3% of Bi<sub>2</sub>O<sub>3</sub>, 0 to 3% of Ga<sub>2</sub>O<sub>3</sub> and 0 to 1% of Sb<sub>2</sub>O<sub>3</sub>, the total content of BaO, SrO, KaO and MgO is 0 to 3% by weight, and the total content of NagO, KaO and LigO is 0 to 1% by

The optical glass II of the present invention is a borosilicate glass comprising at least one selected from La2O3, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> or Yb<sub>2</sub>O<sub>3</sub> and at least one selected from ZrO<sub>27,40</sub> Ta2O5 or Nh2O5, wherein the weight ratio of the total content of La2O3, Gd2O3, Y2O3 and Yb2O3 to the total content of SiO2 and B2O3 is from 3.2 to 5, and the weight ratio of the total content of ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is from 1.1 to 1.5, the boroslicate glass having a refractive index nd of at least 1.875 and an Abbe's number vd of at least 39.5.

The weight ratio of the total content of LigO3, Gd2O3, Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> [( $L_{12}O_3+Gd_2O_3+Y_2O_3+Yb_2O_5$ )/(SiO<sub>2</sub>+B<sub>2</sub>O<sub>5</sub>)] is from 3.2 50 to 5, preferably from 3.2 to 4.5, more preferably from 3.2 to 4, still more preferably from 3.2 to 3.5.

Further, the weight ratio of the total content of ZrO2. Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>  $[(Z_1O_2 + I_2O_3 + Nb_2O_3)/(S_1O_2 + B_2O_3)]$  is from 1.1 to 1.5, 55 preferably from 1.2 to 1.3.

While the above optical glass II has a refractive index nd of at least 1.875 and an Abbe's number vd of at least 39.5, it can exhibit a glass transition point Tg of 700° C. or lower.

The optical glass III of the present invention is a boro- 60 silicate glass comprising at least one selected from La2O3, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>5</sub> or Yb<sub>2</sub>O<sub>5</sub> and at least one selected from ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub> and containing ZnO, wherein the weight ratio of the total content of La2O2, Gd2O2, Y2O3 and Yb2O3 to the total content of  $SiO_2$  and  $B_2O_3$  is from 2 to 5, the 65 weight ratio of the total content of ZrO2, Ta2O5 and Nb2O5 to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> is from 0.5 to 3 and

the weight ratio of ZnO to the total content of SiO2 and B2O3 is at least 0.14, the borosilicate glass having a refractive index and of at least 1.875 and an Abbe's number vd of at least 39.5.

In the optical glass III, the weight ratio of ZnO to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> [ZnO/(SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>)] is at least 0.14, preferably from 0.14 to 2, more preferably 0.18 to 1.5, still more preferably 0.2 to 1. Further, the weight ratio of the total content of  $L_2O_2$ ,  $Gd_2O_3$ ,  $Y_2O_3$  and  $Yb_2O_3$  to the total content of  $SiO_2$  and  $B_2O_3$  [( $L_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$ ). (SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>)] is from 2 to 5, preferably 2.5 to 4.5, more preferably 3 to 3.5.

Further, the weight ratio of the total content of ZrO<sub>2</sub>, TagO<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> to the total content of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>  $[(Z_1O_2 + Ta_2O_5 \times Nb_2O_5)/(S_1O_2 + B_2O_3)]$  is from 0.5 to 3, preferably from 0.8 to 2, more preferably from 1 to 1.5.

While the above optical glass III has a refractive index ad of at least 1.875 and an Abbe's number vd of at least 39.5, it can exhibit a glass transition point Tg of 700° C. or lower.

As a preferred glass composition, the above optical glasses  $\Pi$  and  $\Pi$  has a glass composition comprising, by % by weight, 3 to 10% of SiO2, 7 to 15% of B2O3, 0 to 5% of GeO2, 0 to 15% of ZnO, 30 to 60% of La2O3, 0 to 30% of Gd2O3, 0 to 10% of Y2O3, 0 to 5% of Yb2O3, 2 to 8% of ZrO2 and 13 to 19% of Ta2O3, wherein the total content of SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> is 14 to 20% by weight, the total content of B<sub>2</sub>O<sub>2</sub> and ZnO is at least 9% by weight and the total content of La<sub>2</sub>O<sub>2</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and Yh<sub>2</sub>O<sub>3</sub> is 50 to 60% by weight, and further wherein the total content of the above components exceeds 95% by weight and the glass composition contains 0 to 1% by weight of Li-O and 0 to 3% by weight of Nh2O5-

Each component of the above glass composition is as explained with regard to the glass composition (a) in the above optical glass 1.

Further, the optical glass IV of the present invention is an optical glass having a composition comprising, by 56 by weight, 3 to 10% of SiO2, 7 to 15% of B2O3, 30 to 60% of La2O3, 2 to 8% of ZrO2 and 13 to 19% of Ta2O5, wherein the total content of SiO2 and B2O3 is 14 to 20% by weight. and the total content of the above components is at least 95% by weight.

In the above optical glass IV, preferably, part of La-O-io replaced with Gd2O3 and/or Y2O3, the content of Gd2O3)'s 0 to 30% by weight, the content of Y2O3 is 0 to 10% by weight, and the glass has a glass transition point Tg of 700° C. or lower.

In the optical glass IV, preferably, ZnO is contained in an amount of 0 to 15% by weight and the total content of ZnO and B2O3 is at least 9% by weight. In the optical glass IV, particularly preferably, part of La2O2 is replaced with Gd2O3 and/or Y2O3, the content of Gd2O3 is 0 to 30% by weight. the content of Y2O3 is 0 to 10% by weight, the content of ZnO is 0 to 15% by weight, the content of Nb<sub>2</sub>O<sub>5</sub> is 0 to 3% by weight, the content of Li-O is 0 to 1% by weight, and the glass has a glass transition point Tg of 700° C, or lower, In the optical glass IV, a reason for limitation of the amount range of each component and a preferred amount range of each component are as explained in the glass composition (a) in the above optical glass I.

According to the present invention, there is also provided a preform made of any one of the above optical glasses I to IV, and there is also provided an optical product made of any one of the above optical glasses I to IV.

The above glass preform can be produced by melting raw materials for any one of the above optical glasses I to IV and pre-shaping a molten glass by cold- or hot processing.

The above optical product can be produced by a process comprising the steps of melting raw materials for any one of the above optical glasses I to IV and directly press-molding a molten glass. Alternatively, the above optical product can he practiced by a process comprising the steps of re-heating the above glass preform to a temperature suitable for pressmolding (temperature to attain a viscosity of 104 to 107 Pais), e.g., approximately \$50° C., to soften the preform, and press-molding the preform.

The above processes may include the step of annealing 10 the press-molded article of the glass after the step of directly press-molding a molten glass or after the step of pressmolding the glass preform. The above annealing of the molded article of the glass can be carried out at a temperature around the glass transition point thereof, preferably, in 15 a temperature range within ±20° C. from the glass transition point. In the present invention, the temperature for the annealing can be set at 720° C, or lower, and it can be set at a 700° C, or lower for some glass compositions.

In the above manner, optical products such as a lens and 201 a prism can be efficiently produced.

The optical glass of the present invention is a highrefractivity low-dispersion glass having a low temperature glass. Therefore, the optical glass of the present invention obviates any annealing or re-heat pressing at a particularly high temperature, so that the optical glass can be stably produced.

The present invention will be explained more in detail 30 with reference to Examples, while the present invention shall not be limited by any of these Examples.

#### **EXAMPLES 1-10 and COMPARATIVE** EXAMPLES 1 and 2

Powdery raw materials of carbonate, nitrate, hydroxide, oxide, and the like were provided for forming a glass 10

composition shown in each Example in Tables 2 to 4, and the raw materials were fully mixed. Then, the mixture was placed in a platinum crucible, melted in a furnace set at 1,400° C., stirred and refined, and the molten glass was cast into a frame made of iron pre-heated to a proper temperature, maintained at a temperature around Te for 2 hours and then gradually cooled to give an optical glass.

The thus-obtained optical glasses were measured for properties by the following methods. Tables 2 to 4 also show the results.

#### (1) Refractive index [nd] and Abbe's number [vd]

An optical glass was produced by cooling a molten glass at a temperature-decreasing rate of 30° C./bour and measured.

#### (2) Glass transition point Tg

An optical glass was measured with a thermo-mechanical analyzer at a temperature elevation rate of 4° C/minute.

#### (3) Liquidus temperature [L.T.]

Aglass was placed in a platinum crucible having a volume for viscous flow as compared with a conventional optical 25 of 50 ml, the crucible with a glass in it was covered and maintained in a furnace at a predetermined temperature for 2 hours and cooled. Then, an inside of the glass was observed through a microscope having a magnification of 100 times, and the liquidus temperature of the glass was determined on the basis of whether or not a crystal was formed. The above temperature was changed at intervals of 10° C.

#### $(4) \lambda 50$

A polished sample having a thickness of 10 mm was measured for a spectral transmittance, and a wavelength (nm) at a transmittance of 80% was determined.

TABLE 2

		Example			
		1	2	3	4
Glass	SiO <sub>2</sub>	7.3	7.3	7.3	7_3
Сотро-	B <sub>2</sub> O <sub>3</sub>	8.4	9.4	7.6	9,4
sition	GeO <sub>2</sub>	O	n	0	o
(wi %)	$(SiO_7 + B_2O_3)$	(15.7)	(16.7)	(14.9)	(16.7)
	$(SiO_2 + B_2O_3 + GeO_2)$	(15.7)	(16.7)	(14.9)	(16.7)
	240	2.2	5.0	11.0	5,0
	$(B_2O_3 + 7\pi O)$	(30.6)	(14.4)	(18.6)	(14.4)
	La <sub>2</sub> O <sub>3</sub>	47.8	55.N	41.6	45.8
	ເປັນ,	10.0	0	10.0	10.0
	Y <sub>2</sub> Q <sub>1</sub>	o	O	0	O
	Yb2O1	υ	Ω	0	0
	(Lit-O, + Gd-O, + Y,O, + Yh,O,)	(57.8)	(55.8)	(81.6)	(5.83)
	ZrO:	5.2	5.2	5.2	7.7
	Tc_0,	14.9	15.9	15.9	13.9
	(Sub-lotal)	(95.8)	(98.6)	(34,6)	(98.6)
	Nh <sub>2</sub> O <sub>3</sub>	ง.ส	13.8	(1.4	1.2
	WO,	0	Ð	O	0
	A:,O <sub>3</sub>	2.6	1).4	0.4	U
	Bi <sub>2</sub> O <sub>2</sub>	Ú	9	O	a
	BaO	O	Ω	0	0
	O <sub>1</sub> Z	ŋ	ŋ	Ü	U
	Li.O	0.6	n	o	0
	S6 <sub>2</sub> O <sub>3</sub>	0.2	0.2	0.2	0.2
ZeO/(S:0	0, + B <sub>2</sub> O <sub>3</sub> )	0.14)	0.299	0.738	0.29
	$-\mathbf{G}\mathbf{d}_{2}\mathbf{O}_{3}+\mathbf{Y}_{2}\mathbf{O}_{3}+\mathbf{Y}\mathbf{h}_{2}\mathbf{O}_{3}).$	3.682	3,241	3,4(13	3.34

11

TABLE 2-continued

		Example			
		1	2	3	4
P10-	+ ZrO <sub>2</sub> + Tb <sub>2</sub> O <sub>5</sub> )/(SiO <sub>2</sub> + B <sub>2</sub> O <sub>3</sub> ) Liquidus temperature	1.331 1390	1.311	1,470 1290	1,335 126)
reatics	[UT.] (*C.) Refractive index [nd]	1.83	1.80	1.50	1.89
	Abite's number [vd] Gless transition point	4(),8 692	40.8 <del>69</del> 9	39.6 6 <b>3</b> 9	40.7 697
	[Tg] (* Cl) λ80 (nm)	47]	450	467	450

TABLE 3

			H.XA	mple	
	·	5	tı.	7	ж
Clra	SiO,	6.7	6.7	7_3	8.3
Compo-	B,O,	10.8	10.8	8,4	9.2
silion	GeO <sub>2</sub>	0	0	g	Ú
(wi %)	$(SiO_2 + B_2O_3)$	(17.5)	(17.5)	(15.7)	(17.5)
	(SiO, + B,O, + GeO,)	(17.5)	(17.5)	(15.7;	(17.5)
	ZnO	3.2	4,5	4.5	`32
	$(B_2O_3 + Z_4O)$	(14.0)	(J5.3)	(12.9)	(13.4)
	la <sub>2</sub> O <sub>3</sub>	41.7	41.6	37,8	47.2
	Cd,O,	10.0	9.6	18.0	10.0
	Y.O,	6.0	3.8	a	Ū
	YÑ.Ô.	0	0	3	Ô
	$(L_{12}O_{3} + Gd_{2}O_{3} + Y_{2}O_{3} + Yb_{2}O_{3})$	(57.2)	(55.2)	(55.8)	(57.2)
	7,0,	` 5.2	` 5.2	5.2	4.2
	Tu,O,	15.9	15.9	13.9	16.9
	(Sub-total)	(99.0)	(58.3)	(95.1)	(99.0)
	Nh <sub>2</sub> O <sub>5</sub>	์ น.ฮ	1_3	9	0.8
	wo,	0	0	1.8	ė
	Al-O.	υ	o	1.9	e
	Bi-O,	O	Ü	1.6	ō
	BaO	á	Ŏ	0	ò
	SiO	a	ò	ā	ė
	H <sub>2</sub> O	0	0.2	9	ō
	Sh.O.	0.3	0.2	0.3	0.2
ZaO/(SiG	$O_2 + B_2O_3$	0.133	0.257	0.387	0.183
	Gd <sub>2</sub> O <sub>2</sub> + Y <sub>2</sub> O <sub>2</sub> + Yh <sub>2</sub> O <sub>3</sub> )/	3.259	3.154	3.554	3.260
(SiO. +					
	+ ZrO <sub>2</sub> + To <sub>2</sub> O <sub>3</sub> )/(SiO <sub>4</sub> + B <sub>2</sub> O <sub>3</sub> )	1.251	1,280	1.517	1251
Y10-	Liquidus temperature	1260	1:250	1290	1270
реліся	[LT.] (°C.)				
<b>,</b>	Refrective index [ad]	1.83	1.85	1.88	1.98
	Aboc's number [vd]	41.2	<b>-0.</b> 9	40.5	41.0
	Glass transition point	699	572	707	715
	[Te] (" C)				- 4.
	차이 (am.)	443	464	<b>45</b> 5	450

TABLE 4

_					
		Example		CEx.	
		9	30	1	2
Glass	SiO.	5.9	ó,7	9.3	9.8
Compo-	B <sub>2</sub> O <sub>3</sub>	12.6	9.7	3.4	14.7
sil.on	GeO.	a	1.5	0.5	Ú
(WT 76)	$(SiO_2 + H_2O_3)$	(18.5)	(76.4)	(17.7)	(244)
-	(SiO, + BoO, + GrO.)	(18.5)	(17.9)	(13.2)	(24.5)
	ZnO"	Ò	3.2	9	4.5
	$(B_1O_3 + Z_0O)$	(120)	(12.9)	(8.4)	(19.2)
	ln,O,	43.3	42.5	43.8	30.2
	Gd <sub>2</sub> O <sub>3</sub>	11.0	10.0	14.0	7.6
	Y.Ö,	5.0	4.0	ŋ	3.8
	Yb <sub>2</sub> O <sub>3</sub>	2.0	U	a	
	$(I_{D_2}O_3 + Go_2O_3 + Y_2O_3 + Yo_2O_3)$	(59.2)	(56.5)	(57.8)	(48.2)
	20.	5,4	5.2	5.2	5.2
	Th <sub>2</sub> O <sub>4</sub>	15.9	15.9	13.0	15.9

12

13

TABLE 4-continued

	<u>[:xn</u>	mple		Бх.
	y	10	1	2
(Sub-rotal)	(79.0)	(98.7)	(95.7)	(28_3)
Nb <sub>2</sub> O <sub>3</sub>	0,6	`0,8´	່ວ໌	1.3
wo, "	. 0	o	1.8	ē
ړ <b>ا</b> ړ	0	U	1.9	1)
Bi <sub>2</sub> O <sub>1</sub>	v	0	1.0	Ú
BaO T	0	70	4	Ū
SrO	0	U	· 0	ij
Li-O	O	Ü	G.	0.2
Sb <sub>2</sub> O <sub>3</sub>	0.2	0.2	0.2	0.2
2:0/(SiO. + B.O.)	Q	0.195	41	0.1%4
(La.O. + Gd.O <sub>3</sub> + Y.O <sub>4</sub> + Yb.O <sub>3</sub> )/ (SiO <sub>2</sub> + B <sub>2</sub> O <sub>2</sub> )	3.220	3.445	3.266	1.967
$(Nb_2O_3 + NzO_2 + Tb_2O_3)/(SiO_1 + B$	<sub>7</sub> O <sub>5</sub> ) 1.194	1.335	1.677	6,914
Pro- Liquidus temperature perties [L.T.] (° C.)	1280	12 <b>7</b> 0	1290	1240
Refractive index [nd]	1.8%	1.28	1.88	1,86
(by) rediann a reddA	41.2	41.1	40.7	40_3
Glass transition point	70.8	707	735	690
Х90 (эт)	+4+	460	460	440

CEx. - Comparative Example

As shown in Tables 2 to 4, the glasses of the present invention have a refractive index nd of at least 1.875 and an Alihe's number v of at least 39.5, and it is seen that the glasses in Examples 1 to 6 have a glass transition point Tg of 700° C, or lower and that the glasses in Examples 7 to 10 30 have a glass transition point Tg of 707 to 713° C.

In the glass in Comparative Example 1, the weight ratio of  $(Nh_2O_5+ZrO_2+Ta_2O_5)/(SiO_2+B_2O_5)$  is 1.079 or less than 1.2, and the glass has a high glass transition point Tg of 735° C. In the glass in Comparative Example 2, the weight ratio of  $(La_2O_3+Gd_2O_3+Ya_2O_5+Yb_2O_5)/(SiO_2+B_2O_3)$  is 1.967 or less than 3.1, and the glass has a low refractive index of 1.86.

When the optical glass obtained in Example 6 of the present invention was maintained in an electric furnace at 850° C. for 5 minutes, it was sufficiently softened. The optical glass obtained in Comparative Example 1 was hardly softened. This difference shows that the optical glass of the present invention can be re-heat pressed at a lower temperature than a conventional optical glass.

#### EXAMPLE II

Raw materials were melted in a silica crucible or a platinum crucible for forming the glass composition in each of Examples 1 to 10, and glasses were formed. Glass blocks so were taken from these glasses and cut to obtain molding glass materials.

Each molding glass material was individually softened under heat until they had a viscosity of 10<sup>4</sup> to 10<sup>7</sup> Pars, introduced into a mold having a molding surface corresponding to an optically functional surface of an optical product as an end product, and press-molded to give glass molded materials. Then, the glass molded materials were respectively annealed at glass transition points Tg thereof, to produce optical products.

#### EXAMPLE 12

Raw materials were melted in a silica crucible or a platinum crucible for forming the glass composition in each of Examples 1 to 10. Each molten glass was respectively 65 adjusted to have a viscosity of at least 0.3 Pars and flowed down from a feeder, and a predetermined amount of each

glass that had flowed down was cast into a mold and press-molded to give glass molded materials. Then, the glass molded materials were respectively annealed at glass transition points Tg thereof, to produce optical products.

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Effect of the Invention

The optical glass of the present invention is a highrefractivity low-dispersion glass having a low temperature for viscous flow, so that it serves to attain stable production of optical products without annualing or re-heat pressing at particularly high temperatures.

What is claimed is:

1. An optical glass having a refractive index not of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition temperature of 700° C. or lower and having a composition comprising, by % by weight,

6 <del>-</del> 97£	ŝiO <sub>2</sub> ,	,
9-12%	B.O.,	
0−5ti	ຕະດັ້ງ,	
U-15%	ZnO.	
30-60%	La <sub>2</sub> O <sub>3</sub> ,	
በነውቹ	$GJ_{2}O_{3}$	
0–10%	Y_O <sub>3</sub> ,	
0-5%	Yb,O,	
3-8%	7.rO <sub>.</sub> ,	
13-19%	ひっしょ	

the total content of SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>+GeO<sub>2</sub> being 16 to 19%, the total content of B<sub>2</sub>O<sub>3</sub>+ZnO being at least 9%, the total content of La<sub>2</sub>O<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Yb<sub>2</sub>O<sub>3</sub> being 50 to 60%, the total content of the above components being at least 95%.

,0\_3% لنړ0

being from 1 to 2.

the weight ratio of ZnO/(SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>) being more than 0 but not more than 2.

the weight ratio of  $(La_2O_3+Gd_2O_3+Y_2O_3+Yh_2O_3)/(SiO_2+B_2O_3)$  being from 2 to 4, the weight ratio of  $(ZrO_2+Ta_2O_3+Nb_2O_3)/(SiO_2+B_2O_3)$  (1)

Nb205

0-3%

9-12 W

-603

2\_20%

0-10%

0-5%

Ì—8% 13-19%

2-5%

#### US 6,818,578 B2

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Nh<sub>a</sub>O<sub>re</sub> and wo.

SiO,.

B.O.

Z.O.

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transition temperature of 700° C. or lower and having a composition comprising, by % by weight,

0–1:e WO,		
· · · · · · · · · · · · · · · · · · ·	€-ô&	SiO <sub>2</sub> ,
wherein the optical glass does not contain H[O <sub>2</sub> ,	9−12%	B <sub>2</sub> O <sub>2</sub> ,
	0-5%	GeO.,
2. An optical glass having a refractive index nd of at least	1~7%	ZnO,
1.875, an Abbe's number vd of at least 39.5 and a glass	39-60%	.ل. د نسا
transition temperature of 700° C, or lower and having a	0 <del>-3</del> 0%	Gd <sub>2</sub> O <sub>3</sub> .
composition comprising, by % by weight.	( <b>►10</b> %	Y.O.,
	0–5%	Yh <sub>z</sub> O <sub>z</sub> ,
	2-8%	ZıŌ <sub>:</sub> . ~
	13-19%	π.jō <sub>s</sub> ,

the total content of SiO2+B2O3+GeO2 being 16 to 19%. the total content of B2O3+ZnO being at least 12%, the total content of La<sub>2</sub>O<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Yb<sub>2</sub>O<sub>3</sub> being 50 to 60%, the total content of the above components being at least 95%.

0-3%	Li <sub>2</sub> O, and
0.5-1.5%	Na,O.

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the total content of SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>+GrO<sub>2</sub> being 16 to 19%, the total content of B<sub>2</sub>O<sub>2</sub>+ZnO being at least 9%, the total content of La<sub>2</sub>O<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Yb<sub>2</sub>O<sub>3</sub> being 50 to 60%, the total content of the above components being at least 95%,

3% LI-U: the weight ratio of ZnO(SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>) being more than 0 30 but not more than 2,

the weight ratio of  $(I.a_2O_3+G_3I_2O_3+Y_2O_3+Yb_2O_3)/$ (SiO\_+B<sub>2</sub>O<sub>3</sub>) to mg tions 3 to 4,

The weight ratio of (ZrO2+Ta2O5 (Nb2O3))(SiO2+B2O3) being from 1 to 2, and 0.5-1.5% No. 0.5

wherein the optical glass does not contain HIO2

3. An optical glass having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition temperature of 700° C. or lower and having a composition comprising, by % by weight,

6–97e	SiQ <sub>2</sub> ,
9-12%	B <sub>2</sub> O <sub>3</sub> ,
9–5∕%	GeO <sub>3</sub> ,
1-7%	7.EO,
30-60%	la₌Ú₃.
D-30%	$Gd_2O_3$
<b>2−10</b> %	Y,Ö,,
D-5%.	Yb.,O.,
3-43	
13-10%	ΖτΟ <sub>.</sub> , Τω <sub>ν</sub> Ω <sub>s</sub> ,

the total content of SiO<sub>2</sub>+B<sub>2</sub>O<sub>2</sub>+GeO<sub>2</sub> being 16 to 19%, the total content of B2O3+ZnO being at least 12%, the total content of La<sub>2</sub>O<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Yb<sub>2</sub>O<sub>3</sub> being 50<sup>-55</sup> to 60%, the total content of the above components being at least 95%,

wherein the optical glass does not contain HfO-

5. The optical glass of claim 1, 2, 3 or 4, which has 0 to 5% of Y<sub>2</sub>O<sub>3</sub>.

6. The optical glass of claim 1, 2, 3 or 4, wherein part of La\_O3 is replaced with Gd2O3 and/or Y2O3.

7. The optical glass of claim 1, 2, 3 or 4, wherein part of LagO3 is replaced with Gd2O3 and/or Y2O3 and the content of LigO is 0 to 1% by weight.

8. A glass preform made of the optical glass recited in claim 1, 2, 3 or 4.

9. An optical product made of the optical glass recited in claim 1, 2, 3 or 4.

10. A process for the production of the optical product recited in claim 9, which comprises the steps of melting raw materials for a glass and directly press-molding a molten

11. The process of claim 10, which further comprises the step of annealing a glass molded material obtained by the 45 press-molding, after the step of directly press-molding a molten glass.

12. A process for the production of an optical product, which comprises the steps of softening the glass preform recited in claim 8, under heat and press-molding the glass preform softened under heat.

13. The process of claim 12, which further comprises the step of annealing a glass molded material obtained by the press-molding, after the step of press-molding the glass

14. An optical glass having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition temperature of 700° C, or lower and having a composition consisting essentially of, by % by weight,

0-3%	Li <sub>s</sub> O.
0-3%	Nb <sub>2</sub> O <sub>2</sub> , and
0-1%	₩O <sub>3</sub>

wherein the optical glass does not contain HIO2 An optical glass having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass

<i>0</i> –9%	SiO <sub>2</sub> ,
9–12 <b>%</b>	B_O,.
0=5%	GeO
3-7%	ZnO,
30-60%	.د(ایدا
0-30%	Gd.O.
U-10°&	Y Ohd 3,

35

40

17

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continued				
		2-59 2-89 13-1996	Υδ.Ο <sub>μ.</sub> 2τΟ., Τα,Ο <sub>φ</sub> .	

the total content of SiO2+B2O2+GeO2 being 16 to 19%, the total content of B<sub>2</sub>O<sub>3</sub>+ZnO being at least 9%, the total content of La<sub>2</sub>O<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>5</sub>+Yb<sub>2</sub>O<sub>5</sub> being 50<sub>-30</sub> to 60%, the total content of the above components being at least 95%,

0-3% Li-O.

the weight ratio of ZnO/(SiO2+B2O3) being more than 0 but not more than 2,

the weight ratio of  $(1.a_2O_3+Gd_2O_2+Y_2O_3+Yb_2O_3)$ (SiO\_+B\_O\_) being from 2 to 1,

the weight ratio of (ZrO2+Ta2O3+Nb2O3))(SiO2+B2O3) being from 1 2,

0-3%	No oc acd
0-1%	WO₁.

15. An optical glass having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition temperature of 700° C. or lower and having a composition consisting essentially of, by % by weight,

6-9%	SiO <sub>2</sub> ,
9-12%	B.O.,
9-5%	GeO₂,
U-7%	ZnO,
3D-60%	Lo <sub>2</sub> O <sub>3</sub> .
2–30%	Qq,'Q,"
D-10%	Y-O <sub>3</sub> ,
<b>0-</b> 5%	Yb.O <sub>20</sub>
2-8%	7xO <sub>22</sub>
13-19%	Ta <sub>z</sub> O <sub>a</sub> ,

the total content of SiO2+B25+GeO2 being 16 to 19%, the total content of B<sub>2</sub>O<sub>3</sub>+ZnO being at least 9%, the total content of Ia2O3+Gd2O3+Y2O2+Yh2O3 being 50 to 45 60%, the total content of the above components being at least 95%,

0-3% Li<sub>2</sub>O,

the weight ratio of ZnO/(SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>) being more than 0 but not more than 2,

the weight ratio of (La2O3+Gd2O3+Y2O3+Yb2O3)/ (SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>) being from 2 to 4, the weight ratio of  $(ZrO_2+Ta_2O_5+(Nh_2O_3)/(SiO_2+(R_{23}))$  being from 1 to 2, and 0.5-1.5% Nb.O.

16. An optical glass having a refractive index ad of at least 55 1.875, an Abbe's number vd of at least 39.5 and a glass transition temperature of 700° C. or lower and having a composition consisting essentially of, by % by weight,

ઇ-9પ્ર	SiO.	
2-124	$\mathbf{B}_{2}\mathbf{O}_{3}$	
0 <b>–5%</b>	GeO,	
1-75	ZnO.	
30-60%	La <sub>2</sub> Ò <sub>3</sub> .	
3-30%	Gid.O.	

-continued

0-10%	Y <sub>2</sub> O <sub>3</sub> ,
0-5%	Yo,O,.
2–8%	ZrO <sub>2</sub> .
13194	$T_{\Delta_2}O_{\Delta}$ ,

the total content of SiO\_+B\_O\_+GeO\_ being 16 to 19%. the total content of B2O3+ZnO being at least 12%, the total content of LagO<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Yb<sub>2</sub>O<sub>3</sub> being 50 to 60%, the total content of the above components being at least 95%.

LiO,

17. An optical glass having a refractive index nd of at least 1.875, an Abbe's number vd of at least 39.5 and a glass transition temperature of 700° C. or lower and having a composition consisting essentially of, by % by weight,

WO.

0-3%

0-3% 0-1%

6 <u>-0</u> 7-	SiO <sub>2</sub> ,
9-12%	$\mathbf{B}_{r}\hat{\mathbf{O}}_{n_{r}}$
0-5%	GeOz.
1-7%	ZnO,
3)-(2)%	رکرشا
0-30%	Gd <sub>a</sub> O <sub>a</sub> ,
0-10%	$Y_2O_3$ ,
0−5:7e	Yo.O.
2=875	ZrŌ <sub>=</sub> ,
15-19%	T≊ <sub>2</sub> Ω <sub>s</sub> ,

the total content of SiO.+B.O.+GeO. being 16 to 19%, the total content of B2O3+ZuO being at least 12%, the total content of La<sub>2</sub>O<sub>3</sub>+Gd<sub>2</sub>O<sub>3</sub>+Y<sub>2</sub>O<sub>3</sub>+Yb<sub>2</sub>O<sub>3</sub> being 50 to 60%, the total content of the above components being at least 95%,

ው- <u>ን</u> ፡ <del>ራ</del>	Li <sub>2</sub> O, and	
0.5-1.5%	Nh <sub>2</sub> O <sub>3</sub> .	
	• •	

- 18. The optical glass of claim 14, 15, 16 or 17, which has U to 5% of Y2O3.
- 19. The optical glass of claim 14, 15, 16 or 17, wherein part of La<sub>2</sub>O<sub>3</sub> is replaced with Gd<sub>2</sub>O<sub>3</sub> and/or Y<sub>2</sub>O<sub>3</sub>.
- 20. The optical glass of claim 14, 15, 16 or 17, wherein part of La2O3 is replaced with Gd2O3 and/or Y2O3 and the 60 content of Li<sub>2</sub>O is 0 to 1% by weight.
  - 21. A glass preform made of the optical glass recited in claim 14, 15, 16 or 17.
- 22. An optical product made of the optical glass recited in 65 claim 14, 15, 16 or 17.
  - 23. A process for the production of the optical product recited in claim 22, which comprises the steps of melting

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raw materials for a glass and directly press-molding a molten glass.

24. The process of claim 23, which further comprises the step of annealing a glass molded material obtained by the press-molding, after the step of directly press-molding a smallen glass.

25. A process for the production of an optical product, which comprises the steps of softening the glass preform

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recited in claim 21 under heat and press-molding the glass preform softened under heat.

26. The process of claim 25, which further comprises the step of annealing a glass molded material obtained by the press-molding, after the step of press-molding the glass preform.